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Calibration of the NDHA N_2O model via respirometric assays

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Nitrous oxide; Nitrification; Respirometry; Calibration; Identifiability

Introduction

Nitrous oxide (N_2O) is a by-product of biological nitrogen removal (BNR) with a strong environmental impact as a greenhouse gas. Process models describing N_2O production allow for the development of mitigation strategies. N_2O can be produced biologically by autotrophic and heterotrophic bacteria under different operating conditions. Thus, the desired N_2O mitigation strategies are specific to the main producing pathway. However, accurately predicting what microbial process contributes more to the total N_2O pool is hampered by parameter uncertainty. Improving experimental designs reduces prediction uncertainties, which will benefit N_2O calibrations.

The novelty of the study resides in improving N_2O-model calibrations with simple yet informative experiments and assess the results by examining sources of uncertainty. The objectives of the study are:

(i) Design of targeted experiments for N_2O model calibration.

(ii) Assess AOB-driven N_2O pathway contributions.

(iii) Critically assess N_2O calibration results.

This work represents a step further in understanding not only N_2O production associated to wastewater treatment but also the biokinetic process models used to describe N_2O emissions. Moreover, precise predictions will facilitate the development of N_2O mitigation strategies for wastewater treatment plants.

Material and Methods

Experimental Design: The aim of the experimental design was to study N_2O production associated to nitrification and the potential heterotrophic and abiotic contributions to total N_2O production during nitrification. Respirometric techniques are shown to yield more precise parameter estimates compared to substrate depletion experiments (Chandran et al., 2008). Thus, the kinetics of NH_4^+, NH_2OH and NO_2^- oxidation were measured via extant respirometry. The origin of the biomass was a long-term operated partial nitritation reactor ($NH_4^+{}_{removal}$ = 82±14%, $NO_2^-{}_{prod}/NH_4^+{}_{removed}$ 85±24%).

Respirometric assays were performed following (Chandran and Smets, 2000) in 400-mL jacketed glass vessels with no headspace. DO, pH and liquid N_2O were continuously monitored and nitrogenous substrates (NH_4^+, NH_2OH, NO_2^-, N_2O) were spiked from concentrated stock solutions.

Model Structure: The NDHA model considers N_2O production from three biological pathways, two autotrophic and one heterotrophic (Domingo-Félez and Smets, 2016).

Importantly, the two autotrophic pathways (NN, ND) are distinguished by two NO-producing processes which merge into a single N_2O-producing process. Heterotrophic contribution was also considered (HD) as it plays an important role in the total N_2O production pool even in systems with high autotrophic activity (Domingo-Félez et al., 2017).

Calibration Procedure: The objectives of the calibration are to:

(i) Describe N_2O production during N-removal in respirometric assays.

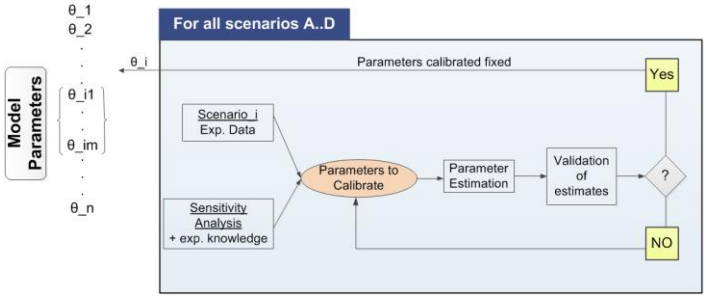
(ii) Estimate the contribution of each pathway to the total N_2O production.

(iii) Quantify the uncertainty of model predictions.

Based on the main oxygen uptake process respirograms were combined in scenarios (Figure 1.1). To identify the influential parameters of model outputs a global sensitivity analysis was performed by linear regression of Monte Carlo simulations (Sin et al., 2009).

For each scenario all possible combinations of sensitive parameters were assessed by increasing the size of the calibration subset to find the largest identifiable subset with the lowest error. The validity of model response, convergence of error minimization, identifiability of parameter estimates and reliability of predictive distributions were also analysed.

The prediction uncertainty of the calibrated model was evaluated by propagating their uncertainty with Monte Carlo simulations. The parameter distribution obtained during calibration was sampled via Latin Hypercube Sampling (n = 400).



Scenario	Spikes	Targeted processes	N_2O pathways
A	NH_4^+	NH_4^+ removal by AOB	NN, ND
B	NH_2OH	NH_2OH removal by AOB	NN, ND
C	NO_2^-	NO_2^- removal by NOB	HD
D	NH_4^+, NH_2OH, NO_2^-	AOB-driven N_2O productio	NN, ND
E	N_2O, NO_2^-	HB-driven N_2O production	HD

Figure 1.1 Schematic of the calibration procedure (left) and experimental design: oxic (A-C) and anoxic (D-E) (right).

Results and Discussion

Quality of experimental design: Firstly, the quality of the experimental design was assessed with default parameters. Results from the sensitivity analysis show that the sequential addition of synthetic substrates contains specific information to individually estimate the biokinetic parameters of each nitrifying step. Moreover, these experiments also carry information about AOB-driven N_2O production (Figure 1.2).

Mapping the uncertainty of model parameters into model outputs showed a higher uncertainty in the predictions of N_2O compared to other nitrogenous species such as NH_4^+, NO_2^- or NO_3^-. N_2O predictions carry a high uncertainty even if N_2O-associated parameters are fixed (0.1% variation). These results highlight the need to consider the uncertainty of all model parameter during N_2O calibration.

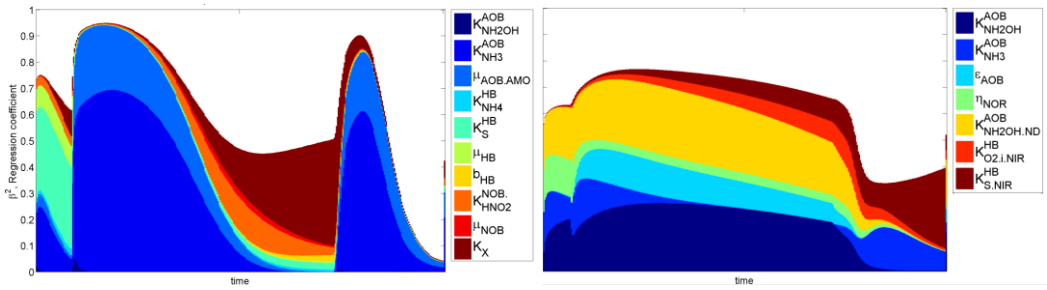


Figure 1.2 Dynamic global sensitivity analysis for a typical respirogram after NH_4^+ spikes for DO (left) and N_2O (right). Only parameters with squared beta values larger than 0.02 at some point of the batch are shown.

DO consumption and N_2O production in respirograms: DO consumption was always positive and proportional to the biomass concentration due to endogenous respiration processes. After substrate addition DO consumption increased, to a much faster rate when NH_4^+ or NH_2OH were added compared to NO_2^- (Figure 1.3), indicating a high AOB abundance compare to NOB or HB, which was confirmed by molecular measurements (data not shown).

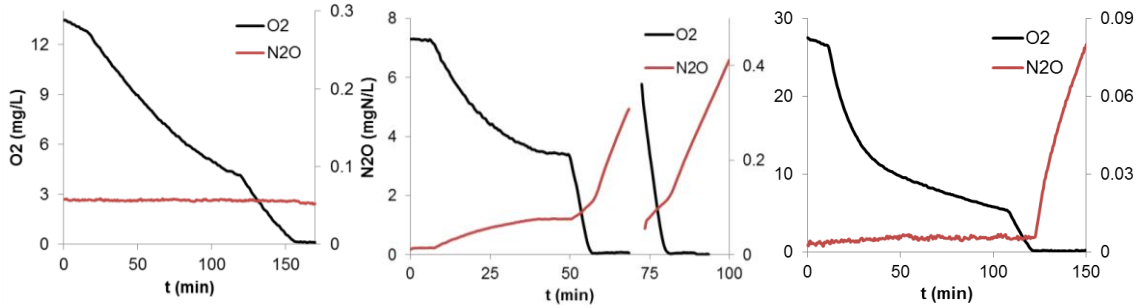


Figure 1.3 DO and liquid N_2O concentrations during respirograms after addition of NO_2^- (left), NH_2OH (middle) and NH_4^+ (right).

NOB-driven N_2O production was not detected during aerobic NO_2^- oxidation or anoxic NO_2^- accumulation (Figure 1.3, left). AOB-driven aerobic NH_4^+ oxidation produced a small amount of N_2O that could be related to incomplete NH_4^+ oxidation to NO_2^-. NH_2OH and NO_2^-, and not NH_4^+, were responsible for a higher N_2O production rate at the onset of anoxia, as NH_4^+ oxidation requires molecular O_2 (Figure 1.3, right). Aerobic NH_2OH oxidation produced more N_2O than NH_4^+ oxidation and, similarly, when reaching anoxia the N_2O production rate increased (Figure 1.3, middle). Results from anoxic experiments (NH_4^+, NH_2OH, NO_2^- and N_2O addition) showed that the NDHA model structure can potentially describe N_2O production from its direct intermediates NH_2OH and NO_2^-.

Model calibration: The NDHA model captured the main DO consuming processes in respirograms after calibrating μ_{NOB}, k_H, μ_{AMO}, $K_{AOB.NH3}$ and $K_{AOB.O2.AMO}$. On the other hand, results for N_2O calibration also showed a good fit but a lower practical identifiability, which is being investigated. The overparameterization of N_2O models could be the reason of the poorer identifiability (three processes are calibrated with one dataset). The contribution of each N_2O-producing pathway was evaluated for the different scenarios (Figure 1.4). For example, during aerobic NH_4^+ oxidation the NN pathway was the main contributor to N_2O production. However, at the onset of anoxia the model predicts a shift in the autotrophic pathways, with a higher ND contribution due to the presence of NH_2OH and NO_2^- under

anoxic conditions that explains the observed N_2O accumulation. These results highlight the importance of N_2O production at low DO and the need to understand the role of intermediates of NH_4^+ removal, specifically NH_2OH and NO, to accurately predict the contribution of each pathway to N_2O emissions (data not shown). Simulation of different DO, NO_2^- and NH_4^+ concentrations indicated that the NDHA can predict a shift between the NN and ND pathways with increasing DO and decreasing NO_2^- while the HD pathway showed a minor contribution to the total N_2O pool.

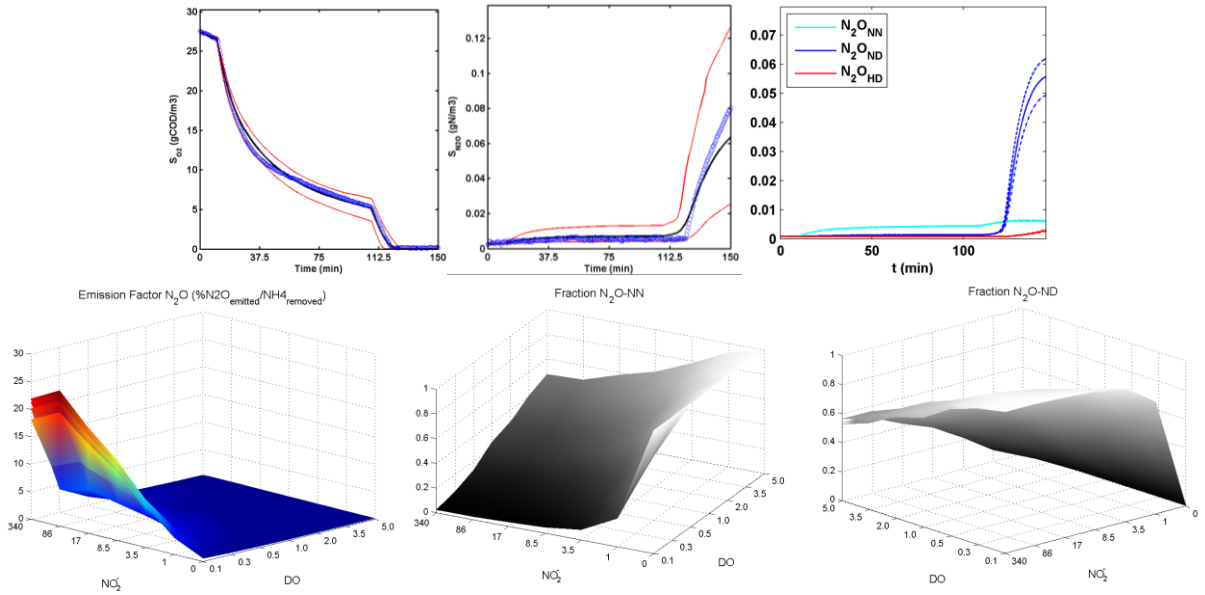


Figure 1.4 Top: Best-fit simulation results and 95% CI of a respirogram after 2 NH_4^+ spikes (Scenario A). From left to right: DO, N_2O, N_2O pathway contributions. Bottom: NDHA model evaluation for varying DO and NO_2^- concentrations. From left to right: N_2O emission factor, NN-pathway contribution, ND pathway contribution.

Conclusions

Respirometric assays are adequate tools to calibrate N_2O models. Optimal experimental design analysis improves the quality and information content of datasets, further improving N_2O model calibrations by reducing prediction uncertainty. The N_2O-associated model parameters showed a lower practical identifiability compared to NH_4^+/NO_2^- removal due to model overparameterization. This uncertainty propagates into the contributions of each N_2O-producing pathway and should be considered during the design of N_2O mitigation strategies.

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